BIOGENIC OR ABIOGENIC ORIGIN OF CARBONATE-MAGNETITE-SULFIDE ASSEMBLAGES IN MARTIAN METEORITE ALLAN HILLS 84001. E. R. D. Scott, Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu HI 96822, USA (escott@pgd.hawaii.edu).

Introduction: McKay et al. [1,2] inferred that the carbonates and included submicrometer grains of magnetite, pyrrhotite and an Fe-S phase identified as "probably griegite" were all biogenic in origin. Their arguments were based on similarities in the compositions, structures, shapes and sizes of these minerals with terrestrial biominerals and the apparent absence of plausible abiogenic origins. Here we compare the carbonate assemblages to possible martian, terrestrial and meteoritic analogs and discuss new and published arguments for and against abiogenic and biogenic origins for these minerals.

Magnetite Fe_3O_4: McKay et al. [1,2] argued on the basis of structure, size, morphology, and chemical composition that the submicrometer-sized magnetites were largely formed intracellularly by magnetotactic microorganisms. Magnetites in ALH 84001 are mostly cuboid, cubo-octahedral, teardrop and irregular in shape [1–3]. A small fraction are elongated rods or ribbons [4] and some are parallelepipedal or hexagonal prisms [5]. Cubo-octahedra and hexagonal prisms elongated along [111], and bullet-shaped crystals formed by asymmetric growth on cubo-octahedra are most characteristic of magnetotactic bacteria [6] and some of these shapes are observed in ALH 84001. However, with the exception of the bullet-shapes, they can also be formed inorganically [7]. Thus although the shapes and sizes of many martian grains are highly suggestive of magnetosomes, except possibly for the tear-drop-shapes, they cannot definitely be identified as crystals from magnetotactic microorganisms. Teardrop-shaped magnetite crystals were originally reported in magnetotactic bacteria: this term was used for oblate spheroids and "tear-drop-shaped cones" [8,9]. However, it is not clear whether the martian teardrops resemble these shapes. Contrary to [4], rod-shaped and twinned magnetites are formed biogenically. However, elongated, ribbon-shaped magnetites and rods with central screw dislocations are very unlikely to be biogenic [4].

Most martian magnetites are single magnetic domains, as observed for magnetotactic bacteria, however the proportion that is superparamagnetic [5] is larger than observed for magnetotactic bacteria [10]. Parallelepipedal particles under 30 nm in length and cuboids under 50 nm in size, which are present in ALH 84001 [1–5], would not have been classified as biogenic if they had been found in a terrestrial sediment. McKay et al. [1] suggested that the smaller, superparamagnetic magnetites resembled those formed extracellularly by the bacterium *Geobacter metallireducens*. However, this organism is not motile and forms magnetites that are irregularly shaped and poorly ordered [10]. There are no reports suggesting that superparamagnetic martian magnetites are more irregular in shape and less well-ordered than single domain magnetites.

Some clusters of elongated magnetites are crystallographically oriented with respect to one another and to the carbonate substrate [11–13]. Epitaxial growth is inconsistent with intracellular growth [12], and extracellular biogenic deposition is also very unlikely as such magnetites are poorly crystalline and irregular in shape. Although biogenic magnetites can be crystallographically oriented on organic substrates with great precision [14], no organism is known to deposit carbonate and magnetite on the same organic substrate. Thus there is no reason to expect epitaxial, biogenic deposition of magnetite on carbonate on any planet.

It is very difficult to understand how magnetites from magnetotactic organisms could have been introduced into a plutonic rock like ALH 84001. It is unlikely that magnetotactic organisms would navigate and swim through a maze of cracks in an igneous rock. It is also very unlikely that any biogenic magnetites from sediments or aqueous environments could be washed into fractures in ALH 84001 by percolating fluids and preferentially trapped during the final stages of carbonate crystallization forming uniformly thin, double shells around carbonates. These factors and the abundance of abiogenic magnetites make it very unlikely that any biogenic magnetites are present in the ALH 84001 carbonates.

Iron Sulfides, Pyrrhotite ($Fe_{0.9}S$), and Griegite (Fe_3S_4): Griegite, pyrrhotite and other iron sulfides can be formed extracellularly by sulfate-reducing bacteria, but these sulfides cannot be distinguished morphologically or chemically from abiogenic sulfides [6]. The absence of isotopically light S indicates that the martian sulfides did not form by this process [15].

Pyrrhotite is not known to form intracellularly in magnetotactic bacteria [16]. In addition some martian pyrrhotites are rounded and polycrystalline and thus could not be magnetic single domains like magnetosomes. Griegite magnetosomes are known, but it is very unlikely that griegite from magnetotactic microorganisms is present in ALH 84001. The particles identified by McKay et al. [1] as griegite are more irregular than known griegite magnetosomes and the identification of griegite is questionable as it was based on the similarity in shape (irregular and approximately rectangular) to a polycrystalline griegite particle formed in soil by non-magnetotactic bacteria. The martian "griegite" particles had pyrrhotite compositions and were unstable in the electron beam, whereas griegite can be studied in the TEM without decomposing [16]. Thus no evidence suggests that the martian sulfides formed biogenically, either intra- or extracellularly.

Carbonate: McKay et al. [1, 2] concluded that the carbonate disks in ALH 84001 were similar in size and shape to some marine, bacterially induced calcite aggregates of submicrometer crystallites [17]. However, martian carbonate crystals appear to be much larger [1]. The unique dumbbell-shaped and brush-shaped aggregates formed by bacteria have not been reported in the martian carbonates.

McKay et al. [2] also compared the martian carbonates to chemically zoned concretions of siderite or ankerite in sedimentary rocks. These compositions are closer to those of the martian carbonates, but terrestrial examples lack the extensive Ca zoning found in small portions of the martian grains. Valley et al. [18] also compared the martian carbonates to concretions but noted that disequilibrium in the terrestrial carbonates may be due to biogenic or abiogenic processes.

Barrat et al. [19] compared the martian carbonates to terrestrial calcite aggregates that may have formed biogenically in the Tatahouine meteorite when it lay in the Saharan desert for 63 years. However, these carbonates are not chemically zoned and lack magnetite rims. Direct evidence favoring a biogenic origin of the martian carbonates is lacking.

Abiogenic origins: Anders [20] suggested that the ALH carbonate assemblages were similar to those in carbonaceous chondrites and had formed abiogenically at low-temperatures. However, McKay et al. [2] noted numerous differences in grain size, composition and texture between martian and chondritic occurrences. Although CI and CM chondrites contain calcite, dolomite and magnesite [21, 22]. there are no chemically zoned grains like those in ALH84001. Magnetites in CI chondrites are larger than those in ALH84001 and those in CM chondrites are rare and not associated with peripheral magnesite. Carbonates in carbonaceous chondrites are also not found embedded in pyroxene and plagioclase glass, as in 84001.

McKay et al. [1] rejected a high temperature origin for the carbonate assemblages in ALH84001 on the basis of C and O isotopic data. However, other authors find that calculated formation temperatures could be 40°–250°C [23] or any temperature in the range 0° to >500°C [24]. The presence of shock formed glass that solidified in situ in fracture zones in ALH 84001 is not consistent with the conclusions of Kirschvink et al. [25] who argued against high temperatures after formation of the fracture zones

Brearley [3] found evidence for high temperatures in the microstructures at carbonate-glass boundaries and suggested that shock-melted plagioclase had heated carbonate. The presence of pores in carbonate around magnetites [1] favors decomposition of Fe-rich carbonate during shock heating, melting or vaporization [3,26]. Such a process also appears consistent with Bradley et al. [4] who concluded that magnetite had condensed above 500°C from a fluid. Rapid heating and cooling in seconds of shock-formed fluids formed above 35 GPa [26] would be consistent with the constraints of Valley et al. [18], who argued against high temperatures over periods of minutes to hours.

Conclusions: Arguments for a biogenic origin for the carbonate, magnetite and iron sulfides in ALH 84001 are absent or very weak: an origin from shock-formed fluids appears much more plausible. Nevertheless, martian sediments and sedimentary rocks should be searched for single-domain magnetites with the unique characteristics of crystals in magnetotactic bacteria. Further searches of carbonates in heavily shocked martian meteorites for grains of biogenic minerals cannot be recommended.

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